

THE REACTIVITY OF DIRECT COAL LIQUEFACTION RESIDS

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SUMMARY

An empirical test for determining the relative reactivity of coal liquefaction resids was developed using the University of Delaware short contact time batch reactor and applied to a suite of fifteen coal liquefaction distillation resids. Conversions of resid to distillate obtained thermally and catalytically are significantly different. Kinetic data, although limited, indicate that a component of the resids is not convertible. An unconvertible insoluble resid component was isolated and its role in resid reactivity is being investigated. A structural model of distillation resids was developed that models the characteristics of the soluble portion of the resids. A reaction model was developed that produces a conversion value for each resid that is within two standard deviations of the experimentally determined values.

BACKGROUND

In the first stage of current two-stage direct coal liquefaction processes, coals are readily converted to non-distillable products (resids) and some distillate. The resid is partially converted to distillate in the second stage of the process. The resid is combined with fresh coal (in a ratio often greater than 1:1, resid:coal) and some vacuum gas oil. This mixture is recycled to the first stage to further convert the resid. Recycled resid is thus a major component of the feed to the process. Its conversion to distillate is a key reaction. Understanding the chemistry of resids and resid reactivity is important to improve direct liquefaction processes design and to reduce production costs for coal liquids.

OBJECTIVES

The three objectives of this study are to understand the chemical characteristics of coal liquefaction resids, the formation of coal liquefaction resids, and the reactivity of coal liquefaction resids. Two questions which were addressed to attain these objectives are: 1) What makes one resid more reactive than another? and 2) What are the effects of process conditions (residence time, temperature, H₂ pressure, catalyst type and loading, coal feed, etc.) on the resid formation and the resid reactivity? The development of an empirical test of relative resid reactivity and the construction of a quantitative model of resid conversion were undertaken to answer these questions.

APPROACH

A suite of 15 coal liquefaction distillation resid samples (Table 1) chosen to represent a wide range of feed coal properties and liquefaction process conditions were characterized with a number of analytical techniques. Elemental analysis, field ionization mass spectrometric analysis, ¹H- and ¹³C- nuclear magnetic resonance spectroscopic analysis, vapor phase osmometry, and Fourier transform infrared spectroscopic analysis were obtained for most samples. Solubility class separations were

accomplished by open column liquid chromatography. A number of other analytical techniques were used and results were reported previously.^{1,2}

The relative reactivity of the resids was determined using an empirical test developed for this purpose.² short contact time batch reactor (SCTBR) was used to react the samples and a thermogravimetric analysis (TGA) method was developed to evaluate the products of reaction and allow for derivation of a conversion value. Design of the SCTBR system and TGA-based analytical procedures were reported in detail previously.³⁻⁷ Tests were made with and without catalyst. All tests were made in tetralin. Heat-up and cool-down times of the resid/tetralin feed mixtures are ca. 0.3 s. Agitation of the slurry is accomplished by an upflow of reacting gas (H₂ or N₂) at 1500 psi (cold). A homogeneous catalyst (Molybdenum naphthenate) was chosen for catalytic tests after trials with heterogeneous catalyst (presulfided Shell 324 Ni/Mo on alumina) proved difficult to use because the required high catalyst loadings resulted in viscous reaction mixtures and poor ash balances. Dimethyldisulfide (DMDS) was used to sulfide the Mo in situ. Tests were made under a range of solvent/resid ratios, residence times, and reaction temperatures. Reported here are results of tests made at 420°C, 30 min, and tetralin/resid = 3/1. Conversion values were determined by separating Tyrolean-soluble and insoluble fractions of the reaction products by filtration. The insoluble fraction was subjected to a simulated distillation method which uses thermogravimetric analysis (TGA) techniques to determine the amount of material boiling below 454°C. The soluble fraction was distilled to remove most of the tetralin, analyzed by gas chromatography to determine the quantity of tetralin remaining, and analyzed by TGA to determine the amount of material boiling below 454°C. Conversion was calculated as follows:

$$\text{Conversion} = \text{tetralin soluble fraction} \times \left(1 - \frac{\text{fraction boiling above } 454^{\circ}\text{C}}{\text{resid soluble fraction}}\right)$$

where the tetralin soluble fraction was determined by ash content of the insoluble resid after hydroprocessing. Resid soluble fraction is the amount of material soluble in tetralin prior to hydroprocessing. Conversion values for all 15 resids are given in Table 2. Values presented in Table 2 were replicated with a standard deviation of 4 wt% (abs.). The large differences (as much as 15 wt% abs.) in conversion among the resids are therefore considered bona fide.

Two of the fifteen resid samples were chosen to study the kinetics of hydroprocessing the resids. The two samples (W259 V131B and W260 V131B) were chosen because they gave the highest and lowest conversion under the standard test conditions (420°C, 30 min, tetralin/resid = 3/1). Tests were made at 435°C to augment tests made at 420°C. Reaction times selected were 5 min and 10 min in addition to the 30 min data already acquired. Conversion leveled off with time, consistent with the presence of a non-convertible component (Figure 1).

Results obtained with the SCTBR indicate that the resid must be soluble in the reaction solvent for hydroprocessing (conversion to 454°C- distillate) to occur. The resids contain ca. 5 to 15 wt% (ash-free basis) tetralin insolubles. This insoluble component is in part responsible for the unconvertible nature of the resid and the leveling off of conversion with time. Several resids were extracted with tetralin to obtain the insoluble fraction. These fractions were hydroprocessed under the same conditions (420°C, 30 min, tetralin/insolubles= 3/1) as the resids. Less than 1 wt% of the insoluble fraction converted to 454°C- product. The study of the insoluble fraction of the resid was expanded by looking

at resids and the process streams from which the resids are derived to determine if the insoluble fraction of the resids formed as an artifact of the high temperature laboratory distillation used to make them. Petrographic analysis and elemental analyses of the insoluble materials indicate that they are, in part composed of unconverted coal macerals. The study of the insoluble portions of the resids is ongoing.

No 1:1 correlation of conversion with product characteristics such as elemental composition, aromatic carbon content or molecular weight were found; nor were correlations found with feed coal rank, sampling location, or other processing conditions. The question of what makes one resid more reactive than another can not be answered by this kind of simple analysis. A computer model capable of testing the sensitivity of resid conversion to the many different characteristics and processing parameters was developed to better determine the effects of resid characteristics and processing parameters on the resid reactivity.

The chemical characterization data and the resid conversion data from catalytic tests made in the SCTBR were used to construct a model of resid reactivity. A structural model was first constructed that represents the soluble portion of the resids. The structural model builds a representative set of molecules using a Monte Carlo technique. In this technique, each molecule is considered to be a set of building blocks or attributes (Table 3). Each of these attributes is described by a probability density function (pdf). The pdf's represent a quantitative probability that the attribute they represent will be less than or equal to a certain value. The pdf's were optimized to produce a set of representative molecules which closely match the experimentally determined soluble resid properties.

A deterministic reaction model was constructed using the optimized pdf's. Each reactive attribute undergoes reaction under a set of reaction rules (Table 4). The reactions result in a change in the relative concentration of the various attributes which, in turn, shifts the pdf's. At any chosen reaction time, the new pdf's can be used to construct a new molecular representation for comparison to the experimentally determined product properties. In the model, any low-boiling (<454°C) component of the resid was accounted for in the prediction of resid conversion. Conversions predicted from resid properties are within two experimental standard deviations of the experimentally determined conversions. (Table 5).

Recommendations

Several avenues of research are recommended to further an understanding of resid conversion. These include determining the impact of different liquefaction catalysts and residence times in different process steps of the liquefaction plant. Determining if catalytically and thermally produced conversion products of resids are chemically different may lead to a better understanding of the reaction pathways for resid conversion. Continued work is recommended to determine if the presence and concentration of insoluble, unreactive compounds in resids can be correlated with resid reactivity. The kinetic studies of resid conversion should be expanded and the data should be used to broaden the applicability of the reaction model.

The structural model and the reaction model incorporate a number of assumptions. More work needs to be done to verify the assumptions and correct or eliminate them. The structural model should be expanded to include terms associated with additional characterization data and should be expanded to

include the insoluble portion of the resid. It is recommended that the reaction model be expanded to include terms associated with additional process conditions.

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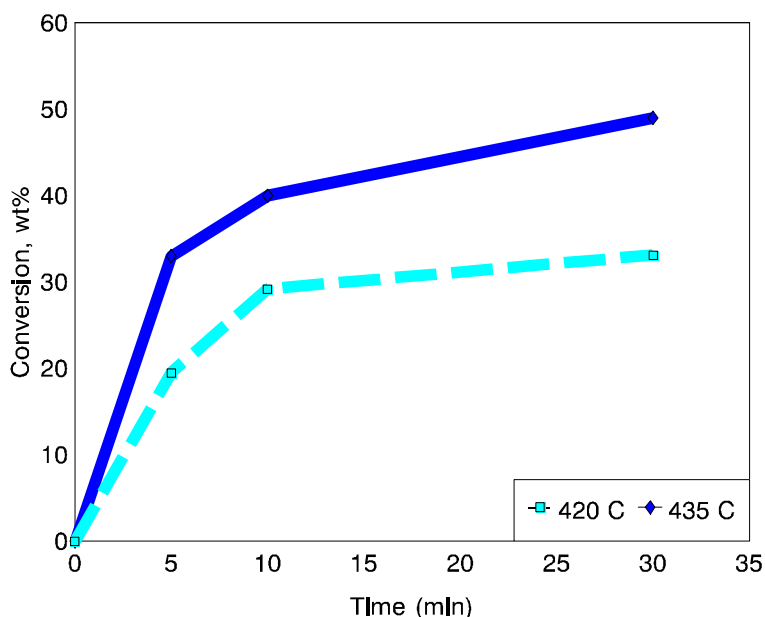


Figure 1. Catalytic Conversion of W259 V131B vs Time at 420°C and 435 °

**Table 1. Sample Set for Resid Reactivity Testing and Sample Analyses
(Moisture and SO₃-Free Ash-Free Basis)**

Plant Run No.	HTI POC01	HTI POC02	Wilsonville Run 259			Wilsonville Run 260		
Feed Coal	Illinois No.6 Burning Star #2 Mine	Wyodak & Anderson Black Thunder Mine	Pittsburgh seam Ireland Mine			Wyodak & Anderson seam Black Thunder Mine		
Sampling location ^a	O-43	O-43	V1067	R1235	V131B	V1067	R1235	V131B
C, wt%	90.70	92.85	90.10	89.99	90.92	86.77	86.61	87.43
H, wt%	8.58	8.72	6.38	6.18	6.50	6.25	5.89	6.35
N, wt%	0.66	0.32	1.05	1.15	1.04	1.10	1.09	1.10
S, wt%	0.34	0.22	1.49	1.50	1.24	1.95	1.82	1.53
O, wt% (by diff)	0.10	2.13	0.98	1.18	0.30	3.93	4.59	3.59
f _a ^b	20.6	18.8	31.6	33.3	31.5	34.0	24.6	33.3
Plant Run No.	Wilsonville Run 261			Wilsonville Run 262			Wilsonville Run 258	
Feed Coal	Illinois No. 6 seam Burning Star # 2 Mine			Wyodak & Anderson seam Black Thunder Mine			Wyodak & Anderson Black Thunder Mine	
Sampling location ^a	V1067	R1235	V131B	V1067	R1235	V131B	V131B	
C, wt%	88.14	87.44	88.39	86.03	85.34	85.84	88.30	
H, wt%	6.53	6.59	6.57	6.75	6.59	6.77	5.61	
N, wt%	1.11	1.19	1.05	0.93	0.99	0.93	1.19	
S, wt%	1.54	1.57	1.05	1.94	1.74	1.73	1.74	
O, wt% (by diff)	2.68	3.21	2.94	4.35	5.34	4.73	3.16	
f _a ^b	30.4	29.4	29.2	24.3	26.0	25.9	38.9	

a) Sampling Location: V1067 = second stage product
R1235 = interstage
V131B = recycle

b) f_a = fraction of aromatic carbon

Table 2. Resid Conversion Data; 420°C, 30 min; tetralin/resid = 3/1

Resid	Conversion, wt%		Resid	Conversion, wt%	
	Thermal	Catalytic ^a		Thermal	Catalytic ^a
HRI ^b POC1 O-43	27.0	47.6	W261 V1067	19.4	42.7
HRI POC2 O-43	22.1	34.3	W261 R1235	16.0	35.3
W ^c 258 V131B	15.0	35.0	W261 V131B	17.1	32.9
W259 V1067	12.9	42.1	W262 V1067	17.7	37.4
W259 R1235	15.9	38.1	W262 R1235	19.6	32.1
W259 V131B	17.7	33.1	W262 V131B	18.2	35.8
W260 V1067	17.8	35.0	a. 3 wt% Mo b. W=Wilsonville pilot plant c. HRI = Hydrocarbon Technologies Inc		
W260 R1235	19.7	35.2			
W260 V131B	21.3	44.6			

Table 3. Some of the Coal Resid Molecular Attributes used in the Structural Model

- Paraffin Length
- Number of Naphthenic Rings
- Number of Sidechains
- Length of Sidechains
- Number of Aromatic Rings
- Number of Naphthenic Rings on an Aromatic Core
- Degree of Polymerization
- Fraction of Heteroatom Cores
- Fraction of Internal Naphthenics
- Fraction of Cores with Phenolic Groups
- Type of Intersheet Linkages

**Table 4. Reaction Rules for Resid Reactivity
(Reaction Carried out in H₂ with Hydrogenation Catalyst)**

- Paraffins crack at the middle of chains.
- Sidechains can crack at ring, alpha to ring, beta to ring, or at middle of chain.
- Sulfur can be removed from bridges and rings to form H₂S.
- Nitrogen can be removed from five-membered rings to form NH₃.
- Oxygen can be removed from bridges and rings to form H₂O.
- Methane can be removed from internal naphthenics.
- Methylene and biphenyl bridges can react.

Table 5. Experimental and Predicted Resid Conversion, wt%

Resid	Conversion, wt%		Difference (absolute)
	Experimental	Predicted	
HTI POC1 O-43	47.6	48.7	1.1
HTI POC2 O-43	34.3	32.8	1.5
W 258 V131B	35.0	37.3	2.3
W259 V1067	42.1	36.6	5.5
W259 R1235	38.1	40.2	2.1
W259 V131B	33.1	34.4	1.3
W260 V1067	35.0	36.9	1.9
W260 R1235	35.2	29.2	6.0
W260 V131B	44.6	36.8	7.8
W261 V1067	42.7	40.4	2.3
W261 R1235	35.3	35.3	0.0
W261 V131B	32.9	39.5	6.6
W262 V1067	37.4	39.8	2.4
W262 R1235	32.1	33.1	1.0
W262 V131B	35.8	38.9	3.1